The Condensation of Methyl β-Chlorovinyl Ketone with Aromatic Diamines

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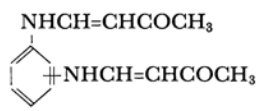
(Received September 11, 1965)

The condensation of methyl β-chlorovinyl ketone (I) with amines such as aniline and *p*-aminophenol has previously been reported from this laboratory,[1] while the reaction of monoamines with I has been reported by Yakubovich.[2] While the reaction of α, β-unsaturated ketone with aromatic diamine is well known,[3] no example involving the condensation of I, an α, β-unsaturated ketone with chlorine on the β-position, with a diamine is found in the literature. During the course of a synthetic investigation of cyclic-conjugated compounds containing nitrogen it, however, became desirable to prepare new condensation products of I with aromatic diamines. This paper is concerned with the reaction of I with aromatic diamines, e. g., *o*-, *m*-, and *p*-phenylenediamines.

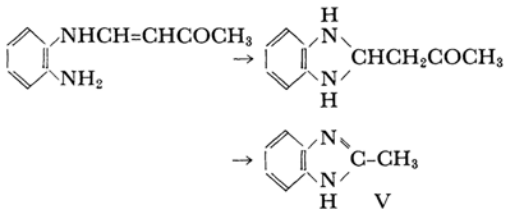


II: *o*-
III: *m*-
IV: *p*-

The reaction of two moles of I with one mole of *o*-phenylenediamine in the presence of potassium carbonate afforded a resinous substance which was sparingly soluble in ether. By the chromatographical fractionation of the resinous substance, a small quantity of crystals was obtained and identified with V on the basis of its elementary analysis and its ultraviolet and infrared absorption spectra. V showed an ultraviolet absorption spectrum

1) G. Inoue, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **79**, 1233 (1958); **80**, 1061 (1959).
2) A. Ya. Yakubovich and E. N. Merkulova, *J. Gen. Chem.* (USSR), **16**, 55; *Chem. Abstr.*, **41**, 91 (1947).
3) a) W. Ried and P. Stahlhofen, *Chem. Ber.*, **90**, 815 (1957). b) J. Davoll, *J. Chem. Soc.*, **1960**, 308. c) G. Bryant and L. V. Heisey, *J. Am. Chem. Soc.*, **71**, 1985 (1949). d) W. Ried and Urlass, *Chem. Ber.*, **86**, 1101 (1953). e) W. Ried and W. Hohne, ibid., **87**, 1181 (1954). f) F. B. Wigton and M. M. Joullie, *J. Am. Chem. Soc.*, **81**, 5212 (1959). g) W. R. Benson and A. E. Pohland, *J. Org. Chem.*, **29**, 385 (1964). h) F. Scotti and E. J. Frazza, ibid., **29**, 1800 (1964).

analogous to that of 2-methylbenzimidazol[4] and, as its infrared absorption maxima, 3400 (ν_{N-H}) and 2950 (ν_{C-H}) cm^{-1}. The formation of V might be explained as follows.



The reaction of two moles of I with one mole of *m*-phenylenediamine or *p*-phenylenediamine in the presence of potassium carbonate gave the expected condensation products, III and IV respectively. The ultraviolet absorption maximum of III appeared at 352 mμ in a neutral solution and at 351 mμ in an acid solution. If the nitrogen atom in the conjugated system of III had been protonated in an acid solution, the maximum of the absorption should move to the shorter wavelength. The preceeding observation that the absorption did not show the hypsochromic shift means that the protonation on the oxygen atom of the acetyl group in III is preferable to that on the nitrogen atom. The similar discussion will be supported by the fact that the ultraviolet absorption maximum of IV was 386 mμ in neutral and 395 mμ in acid solution. The infrared absorption maxima were found at 3400 (ν_{N-H}) and 1640 ($\nu_{C=O}$) cm^{-1} for III and at 3400 (ν_{N-H}) and 1630 ($\nu_{C=O}$) cm^{-1} for IV. These spectral data are consistent with structures III and IV.

The reactivity of III or IV with formaldehyde or benzaldehyde in the presence of piperidine acetate was so small that the aldol condensation products could not be formed. Both III and IV were found to be reasonably stable to sunlight, ultraviolet ray or γ-ray irradiation.

Experimental

All the melting points are uncorrected.

The Reaction of *o*-Phenylenediamine with Methyl β-Chlorovinyl Ketone.—Freshly-distilled methyl β-chlorovinyl ketone (10 g., 0.1 mol.) and *o*-phenylenediamine (5 g., 0.05 mol.) were dissolved in water (50 ml.); to this mixture potassium carbonate (27 g., 0.2 mol.) was then gradually added. The reaction product was resinous and insoluble in ether. The ethanol solution of the product was chromatographed on alumina. From the elution a trace of colorless crystals (V) was obtained; m. p. 176°C.

Found: C, 71.29; H, 5.37; N, 21.07. Calcd. for $C_8H_8N_2$: C, 72.70; H, 6.10; N, 21.20%.

UV: λ_{max}^{EtOH} (ε) 245 (6100), 273 (5900), 279 (6800) mμ, λ_{max}^{acid} 240, 268, 274 mμ, IR: ν_{N-H} 3400, ν_{C-H} 2950, 2850, ν_{C-H} 1360 cm^{-1}.

It was difficult to crystallize most of the resinous substance whose ultraviolet absorption maximum was near 390 mμ. This suggested the formation of II, but the resinous substance could not be sublimed in vacuo (10^{-3}—10^{-4} torr.) with a molecular still. Consequently, this substance must not be II but must be composed of polymers containing a conjugation similar to that of II.

***N*, *N'*-Di-(2-acetylvinyl)-*m*-phenylenediamine (III).**—To the mixture of methyl β-chlorovinyl ketone (10 g., 0.1 mol.) and *m*-phenylenediamine (5 g., 0.05 mol.) in water (50 ml.), potassium carbonate (27 g., 0.2 mol.) was gradually added. The reaction product was extracted with ether, and the ether layer was concentrated and kept in a refrigerator; brown fine cyrstals, 1.35 g., m. p. 195°C, were thus afforded.

Found: C, 68.89; H, 6.46; N, 11.52. Calcd. for $C_{14}H_{16}O_2N_2$: C, 68.83; H, 6.60; N, 11.47%.

UV: λ_{max}^{EtOH} (ε) 352 (41000) mμ, λ_{max}^{acid} 351 mμ.

IR: ν_{N-H} 3400, $\nu_{C=O}$ 1640, ν_{C-H} 1350 cm^{-1}.

***N*, *N'*-Di-(2-acetylvinyl)-*p*-phenylenediamine (IV).**—The reaction mixture of methyl β-chlorovinyl ketone (10 g., 0.1 mol.) and *p*-phenylene diamine (5 g., 0.05 mol.) in the presence of potassium carbonate (27 g., 0.2 mol.) was extracted with ether, dissolved in hot ethanol, and kept at room temperature. After recrystallization, fine orange-yellow needle crystals were obtained, m. p. 193°C.

Found: C, 68.72; H, 6.56; N, 11.48. Calcd. for $C_{14}H_{16}O_2N_2$: C, 68.83; H, 6.60; N, 11.47%.

UV: λ_{max}^{EtOH} (ε) 386 (47000) mμ, λ_{max}^{acid} 395 mμ.

IR: ν_{N-H} 3400, $\nu_{C=O}$ 1630, ν_{C-H} 1360 cm^{-1}.

The Attempted Condensation of III or IV with Aldehydes.—Equimolecular mixtures of III or IV and formaldehyde or benzaldehyde were kept at room temperature or heated under reflux in the presence of piperidine acetate or piperidine. From each reaction mixture III or IV and aldehyde were recovered.

The Change of III or IV with Sunlight, Ultraviolet Ray or γ-Ray Irradiation.—III and IV were stable to sunlight for a week, and to the ultraviolet rays of a high-pressure mercury lamp for two days. The γ-ray irradiation of III and IV, with a total dose of 5×10^7 r./hr. and a dose rate of 1.5×10^7 r./hr. showed little change in the ultraviolet absorption spectrum. The precise results will be reported elsewhere.[5]

4) R. Huisgen and H. Rist, *Ann.* **594**, 161 (1955).

5) Y. Kurabayashi, K. Kurihara, Y. Omote, *J. Vacuum Chem. Soc. Japan* (*Shinku Kagaku*), in press.